

*Transformation of minerals of the montmorillonite family into 10 Å. micas.*¹

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IN his work on the mineralogy of soils colloids G. Nagelschmidt,² suggests the possibility of a reversible change of the type

montmorillonite \rightleftharpoons illite \rightleftharpoons muscovite.

We have attempted to establish experimentally the existence of this transformation following fixation or departure of the potassium from between the fundamental structural sheets of the mica type. The initial material was montmorillonite from Camp Bertaux, Morocco, separated from its impurities by sedimentation. As it was evident *a priori* that the alteration of montmorillonite into illite necessitates (1) saturation of the base-exchange capacity of the minerals by potassium, and (2) the departure of the layers of water from between the structural sheets of the montmorillonite, we finally, after several attempts, were led to make use of the following technique.

The sample of montmorillonite was first of all saturated with potassium by treatment with a normal solution of KCl; then, after decantation of the excess of the solution, 200 c.c. of normal KOH solution were added per 4 grams clay. It was boiled 8 hours and, in order to avoid loss of material by projection, it was convenient to place the suspension in an Erlenmeyer flask attached to a vertical cooling column. The product was then filtered, washed, and dried for one hour in an oven. After this treatment the clay already showed a sandy consistency.

¹ Read August 27, 1948, at the meeting of the Clay Minerals Group at the International Geological Congress, London, under the title: S. Hénin, Transformation des minéraux de la famille des montmorillonites en phyllites à 10 Å. (Internat. Geol. Congr., Volume of Titles and Abstracts, 1948, p. 128). A portion of the paper had appeared as a preliminary note: S. Caillère, S. Hénin, and S. Mériaux, Transformation expérimentale d'une montmorillonite en une phyllite à 10 Å type illite. Compt. Rend. Acad. Sci. Paris, 1948, vol. 226, pp. 680-681. [M.A. 10-368.] Translated by Dr. D. M. C. MacEwan.

² G. Nagelschmidt, The mineralogy of soil colloids. Techn. Commun. Imp. Bur. Soil Sci. Harpenden, 1944, no. 42. [M.A. 9-76.]

Nevertheless it was necessary to repeat the operation three and four times to obtain a substance which, when examined with X-rays in the air, gave a diagram showing the following characteristics.

The principal spacing is 10.2 \AA . and its intensity is weak in comparison with the other lines of the diagram. A third-order line at 3.2 \AA . is also observed, which has essentially the same intensity as the corresponding line of illite. If one makes a diagram of the same substance, but this time immersed in the mixture of water and glycerol, no change is observed. We have, therefore, a stable mineral with 10 \AA . spacing showing the characteristics of illite.

However, on treating this product for three days with a mixture of $2N\text{-CaCl}_2$ and 10 c.c. $N/10\text{-HCl}$ a product is obtained which on air drying shows a principal spacing of 11.7 \AA . in the form of a rather diffuse ring. On the other hand, a diagram of this substance steeping in the water-glycerol mixture does not show any large spacing line, or at the most it is possible to make out a circular veil corresponding to all possible spacings between 10 and 17 \AA . This series of results allows the conclusion to be drawn that the treatment we used blocks the expansion of the montmorillonite and leads to a product with properties similar to illite. The partial reversibility of the change produced by treatment with calcium salts shows, however, that this result is incompletely attained. We shall return to this subject later.

We have also tried treatment with potassium carbonate, potassium chloride, potash of several concentrations, ammonia, and soda; but only the treatment just described leads to a fairly constant result. We have never obtained it with other cations than potassium, and only when the latter was in the form of KOH of different concentrations; although with more concentrated solutions, for example $5N$, the result is much less certain and the time of treatment must be reduced in order to avoid dissolving too great a quantity of the initial mineral. We may note further that on making an X-ray diagram in air of the sodium product prepared by boiling in $N\text{-NaOH}$ it shows a principal spacing of 12 \AA . and its higher orders.

We have also applied the treatment to a nontronite from Behenjy, Madagascar, and the result was essentially the same as that given by the montmorillonite. However, the nontronite thus treated is a little less stable than the montmorillonite, for it is found that the ring corresponding to the principal spacing although remaining at about 10 \AA . becomes slightly diffuse on making a diagram of the water-saturated substance. It is, nevertheless, true that the behaviour

established by these experiments seems to hold for the different members of the montmorillonite family.

Verification by thermal methods.

With a view to supporting the results of the X-ray study by other observations, we carried out weight-loss analyses and differential thermal analyses on the initial and treated materials and on bravaisite.

The curves given by the Chevenard thermo-balance, which allows of a continuous recording of the weight of the substance as a function

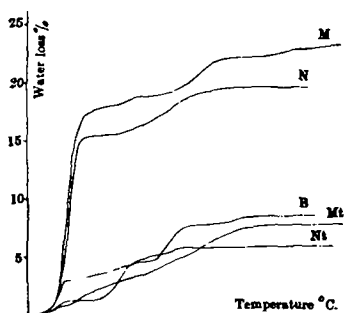


FIG. 1. Dehydration curves.

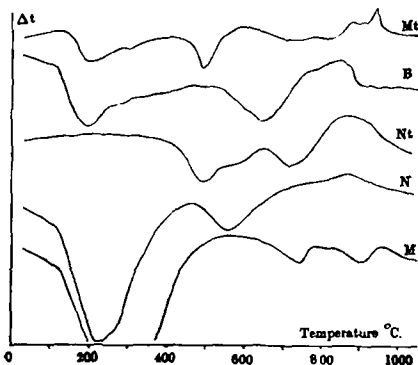


FIG. 2. Differential thermal curves.

Montmorillonite (M), treated montmorillonite (Mt), nontronite (N), treated nontronite (Nt), bravaisite (B).

of the temperature to which it is subjected, are reproduced in fig. 1. The initial samples (curve M, montmorillonite, and N, nontronite) are characterized by a loss of hygroscopic water of the order of 15 %, plus a more or less continuous loss of water of constitution, beginning a little below 300° for nontronite, and a little below 500° for montmorillonite. The bravaisite, on the contrary, shows a small loss of hygroscopic moisture, of the order of 3 %, and the loss of water of constitution shows up around 430°.

The curves corresponding to the treated montmorillonite, Mt, and the treated nontronite, Nt, show a very small loss of hygroscopic water, in accordance with the observed blocking of the structural sheets. The small water loss found with bravaisite is probably due to this mineral being a mixture of a 10 Å. material with a small quantity of 14 Å. material. As regards the loss of water of constitution, it essentially reproduces that of the initial minerals, but with somewhat lower

temperatures, and a more spread-out appearance. Apart from this last characteristic, the curves are obviously similar to the bravaisite one.

The differential thermal analysis, carried out with the Saladin-Le Chatelier apparatus, gave the curves reproduced in fig. 2, the same symbols as before being used. The montmorillonite curve (M) shows three characteristic peaks at 230°, 730°, and 900°. The nontronite curve (N) has two peaks, one at 210°, the other around 550°; finally the bravaisite curve (B) is distinguished by three peaks, one around 200°, much weaker than on the preceding diagrams, a second around 630°, relatively large but rather spread out, and lastly a rounded exothermic peak at 840°.

The treated montmorillonite (Mt) shows a weak endothermic peak at 200°, then a well-marked peak around 490° and finally a flattened exothermic feature around 920°. The treated nontronite (Nt) gives a similar curve but the second endothermic peak is around 500°, further two rounded features around 650° and 850° seem to be due to exothermic phenomena, the latter one corresponding to that of bravasite. Thus, thermal study leads to identical conclusions to those which emerged from the X-ray examination. Finally, we may note that chemical analysis of the treated montmorillonite brings out a potassium content of the order of 5 %, corresponding to that of illite.

Alteration of vermiculite.

In an attempt to further extend the preceding results, we experimented on vermiculite from Corundum Hill, North Carolina. Since this mineral occurs as platelets with dimensions of the order of a centimetre, we thought it would be necessary to reduce it to smaller dimensions. The original platelets were filed, and the resulting product sieved with a no. 100 sieve. Five grams of this powder were put into a porcelain pot with 500 grams of steel ball-bearings, and a sufficient quantity of water to form a paste. The pot was put on to an end-over-end shaker, which was operated for 30 hours. The distance covered in the interior of the pot was of the order of 20 kilometres. The bigger part of the product forms a stable suspension in water, and it may be assumed that the particles had a diameter smaller than 2 μ . The product was then purified to remove the iron introduced by the grinding, by boiling for $\frac{1}{2}$ hour in $N/4\text{-H}_2\text{SO}_4$.

The X-ray diagram obtained with this product did not differ essentially from the type vermiculite diagram. The procedure already described was applied to this substance. The results are not so clear as for the

montmorillonite, but an identical alteration is shown, characterized by a broadening and weakening of the central ring, which became much hazier. Its mean spacing is of the order of 11 Å. Although this result is not so conclusive as one could have wished, it still remains very probable that here also we have obtained a closing-up of some of the structural sheets. We may recall that J. W. Gruner¹ succeeded in obtaining such a closing-up with vermiculite by a combined treatment with hydrogen peroxide and ammonia; but that he did not obtain this result using other cations, in particular potassium, except by heating to 300°.

We have mentioned this last experiment, firstly, because it shows the generality of the alteration observed, and secondly, because it was carried out starting with a well-crystallized mineral. This proves that it is possible to study in the laboratory alterations which can go on in nature, and to make an experimental approach by mechanical and chemical alteration to the formative processes of sedimentary rocks.

In the present state of our experiments it is still difficult to understand the mechanism of the changes just described. Clearly, by bringing potassium ions in between the montmorillonite sheets, there is a tendency to approach the mica structure, but this fact alone does not explain why simple saturation in the cold, following by oven-drying does not bring about the same result. Moreover, if one supposes an alteration of the mineral, and the blocking of the structural sheets by decomposition products, it is not clear why ammonia or soda treatment does not lead to a similar closing-up of the montmorillonite.

We may note also that the quantity of potassium introduced is of the order of the base-exchange capacity, so the alteration can also not be interpreted by a raising of the number of potassium ions fixed; only a more thorough study of these phenomena can clarify the subject.

An attempt to transform mica into montmorillonite.

It may be taken as very probable that mica, by natural weathering, gives products similar to montmorillonite; moreover, we have seen that montmorillonite which has been transformed into mica can open up as a result of chemical treatment. We therefore attempted to bring about this change experimentally, starting either from sheet mica or from illite.

The two micas used, phlogopite and illite, were crushed following the technique described for the vermiculite study. The crushed samples were brought into the colloidal state. All the samples, illite and mica, were first treated by a solution of CaCl_2 and hydrochloric acid as for

¹ J. W. Gruner, *Amer. Min.*, 1939, vol. 24, p. 428. [M.A. 7-479.]

the montmorillonite. Despite the fact that the treatments were lengthened and carried out both hot and cold, or alternated with alkaline treatment, we never obtained results indicating any opening-up of these minerals. We then used vigorous reagents, either 50 % HCl in the cold for 3 days, or hot H_2SO_4 during a variable time, from $\frac{1}{2}$ to 4 hours. In this last case, a certain amount of magnesium sulphate was added to the solution to try to fix some divalent ions between the structural sheets.

The results observed were as follows. The X-ray diagram of sulphuric acid-treated muscovite showed a slight modification of the central line, which tended to become hazy; also, several fine lines disappeared and the diagram approached that of illite. Study of the treated muscovite with the Chevenard balance showed a loss of hygroscopic water of the order of 3 %, which can be attributed to the penetration of water between the mica sheets. With phlogopite, the results were essentially the same, but the number of trials was much less than with muscovite.

Of the two illites used one comes from South Wales and was kindly furnished by G. Nagelschmidt and D. Hicks,¹ the other is a typical sample from Illinois. The sulphuric acid treatments gave products whose X-ray diagrams showed large-spacing lines which were less intense and hazier than for the initial samples. As a result of a series of unfortunate circumstances, the diagrams obtained were rather bad, which did not allow us to observe the higher-order lines of the (00l) series. The treated products, heating to 250° gave a weak but sharp central line. This tends to prove that opening-up of the mineral has occurred, heating having the effect, according to this point of view, of closing the structural sheets, which had been opened up by the treatment; however, it may be possible that the haziness found was due to an alteration product which was decomposed by heating. Thus, from this last series of experiments no very clear conclusion can be brought out.

The results justify us in hoping that it may be possible to open up the mica structure, for the changes brought about are certainly similar to those observed in the opening-up of the 'artificial illite' produced by treatment of montmorillonite. The only positive fact which emerges from these trials is that these minerals can only be opened up with difficulty. We may thus conclude that it is possible to obtain a change of montmorillonite or vermiculite into illite, permitting a study of the physico-chemistry of this alteration, and that the inverse change, of mica into montmorillonite in the laboratory, is very likely to occur also.

¹ G. Nagelschmidt and D. Hicks, *Min. Mag.*, 1943, vol. 26, p. 297.